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The Basis for Developing Samarium AMS for Fuel Cycle Analysis

Bruce A. Buchholz[1*], Steven R. Biegalski[2], Scott M. Whitney[2], Scott J. Tumey[1], and C. Jordan Weaver[2].

   (1) CAMS L-397, LLNL, 7000 East Avenue, Livermore, CA 94551 USA
   (2) Nuclear Engineering Teaching Laboratory, University of Texas, Austin, TX 78741 USA

Modeling of nuclear reactor fuel burnup indicates that the production of samarium isotopes can vary significantly with reactor type and fuel cycle. The isotopic concentrations of ^{146}Sm, ^{149}Sm, and ^{151}Sm are potential signatures of fuel reprocessing, if analytical techniques can overcome the inherent challenges of lanthanide chemistry, isobaric interferences, and mass/charge interferences. We review the current limitations in measurement of the target samarium isotopes and describe potential approaches for developing Sm-AMS. AMS sample form and preparation chemistry will be discussed as well as possible spectrometer operating conditions.

        * Corresponding author. bbuchholz@llnl.gov Office:1-925-422-1739 FAX: 1-925-423-7884

Introduction

Isotopes produced from fission and capture reactions in nuclear reactors vary with reactor fuel, moderator, fuel cycle, operational parameters, and overall reactor design. Some design and operation features produce distinct profiles in the spent fuel or dissolved waste. The isotope profiles can identify the type of reactor, the length of reactor fuel cycle, neutron flux, neutron fluence, and other parameters.

We previously performed fuel cycle modeling to determine which long-lived or stable fission products vary with irradiation history and found the isotopic concentrations of ^{146}Sm, ^{149}Sm, and ^{151}Sm to be illustrative [1]. Isotope ratios of specific elements contained in the waste after spent fuel reprocessing can indicate of the length of the fuel cycle as well as reactor type when sensitive detecting techniques are utilized. It is important to note that isotopic ratios of individual elements are utilized in contrast to ratios of different elements since isotopic ratios are least affected by chemical fractionation that can occur during processing or environmental transport.

Using open source Oak Ridge Isotope Generation and Depletion codes, ORIGEN-ARP and ORIGEN-2.2 [2,3] we modeled fuel cycles in Pressurized Water Reactor (PWR), Boiling Water Reactor (BWR), Canada Deuterium Uranium Reactor (CANDU), and Liquid Metal Fast Breeder Reactor (LMFBR) nuclear reactors [1]. Short, low burnup (1 month) and long, high burnup (18 months typical of a commercial power reactor) fuel cycles were modeled. We assumed 1 year of cooling after removing the fuel from the core for the decay of short-lived isotopes. The ORIGEN codes are a well substantiated set of codes that have been used for decades in nuclear engineering research and reactor fuel management.

The ratios of the rare, long-lived fission product ^{146}Sm to a high yield fission product ^{151}Sm and to a stable isotope ^{149}Sm produced in a typical power PWR with 15 day and 500 day fuel cycles is graphed in Fig. 1. Measurement of stable Sm isotopes by TIMS is reported with a small dynamic range, isotope ratios were on the order of 0.1-10 [4,5]. The use of ICP-MS is now preferred for measuring Sm isotopes in spent nuclear fuel [5-7]. ICP-MS routinely measures stable isotopes at the ppm level, but again has only been used for high abundance stable isotopes. Neither TIMS nor ICP-MS appear capable of measuring ^{146}Sm/^{149}Sm and ^{146}Sm/^{151}Sm to 10^{-9} or lower over a large dynamic range likely to be encountered (see Fig. 1).

The relative isotopic concentrations of ^{146}Sm, ^{149}Sm, and ^{151}Sm are potential signatures of fuel reprocessing, if analytical techniques can overcome the inherent challenges of very low ^{146}Sm concentration, separatory lanthanide chemistry, isobaric interferences, and mass/charge interferences. We review the current limitations in measurement of the target samarium isotopes and describe potential approaches for developing Sm-AMS. AMS sample form and preparation chemistry will be discussed and considerations for spectrometer operating conditions will be briefly suggested.

Sm Sample Processing Options

Producing a high quality sample cathode material suitable for AMS sputter ion sources will likely be the most difficult task in developing Sm-AMS. The starting sample matrix for this application is likely to be an aqueous waste stream, waste organic solvent, spent separatory column, or precipitated solids inside a tank or drum. All of these matrices will be rich in lanthanides and other fission products, not a purified isotopic target typically used in nuclear physics experiments. An initial aqueous chemistry clean-

up step to remove or reduce the soup of elements will need to be done. Luckily,

lanthanide chemistry is well developed and a variety of approaches have been used to

separate Sm from other lanthanides and other trivalent aqueous ions [8-13]. Many

isobars exist in the range of interest. A list of some possible injection isobars capable of

carrying a 1^- charge is provided in Table 1.

Middleton demonstrated intense SmH_2- and SmH_4- beams using a gas cathode, which

flowed H_2 gas over metallic Sm [14]. The gas cathode is not conducive to sample

switching, but suggests that samarium hydride might make a good cathode material.

Several techniques for producing a variety of samarium hydrides for specialized

applications are in the literature. The diffusion of H_2 gas into hot Sm metal [15,16],

production as a thin film layer [17,18] , an organometallic complex [19,20] or a nano-

particle [21] are not readily transferred to typical AMS sample processing. The hydride

is likely to be very reactive with water, and probably not a first choice as a cathode

material if other suitable materials can be found.

SmF_2 and SmF_3 are also possible cathode materials. SmF_3 sputtering targets are

commercially available in semiconductor and vapor deposition applications. Most

halogenated molecules form negative ions well, and F has been useful in the past [22-24].

Recent work at CAMS has focused on SrF_2 cathodes to get improved current over oxide

without the difficult sample prep of the hydride [25]. We believe samarium fluoride may

present a similar compromise compared to samarium hydride, better sample stability at

the expense of current and energy resolution. A variety of procedures for producing

lanthnide fluorides from oxides are in the literature because the trifluoride is a precursor

to metal production [26-28]. The procedure for producing SmF_3 most amenable to batch

processing dissolves Sm_2O_3 in hydrochloric or nitric acid, precipitates the fluoride by adding HF, and dries the precipitate under vacuum or in an inert atmosphere at 300°C to yield anhydrous SmF_3 [27,29].

Tests of output from the LLNL ion source [30] produced up to 300-400 nA of $^{152}SmF^-$ and $^{154}SmF^-$ from cathodes of SmF_3 mixed with Nb metal powder (Table 2). The ion source was operated under typical conditions with a cathode voltage of 9.0 kV and ion currents were measured in an in-line Faraday cup after traversing the 90° bend of our injector magnet. The cathode currents improved over time, starting at about 100 nA and increasing to 300-400 nA over 30 minutes and retaining the maximum current for an additional 40 minutes. We did not attempt to exhaust the samples. The currents of the SmF^- of the naturally occurring Sm isotopes of masses 147,148,149, 150, 152, and 154 were proportional to their natural abundances aside from mass 173 ($^{154}Sm^{19}F$), which was about 20% too high. We did not identify the interference. We checked production of SmF_3^- since there are typically fewer isobars above mass 200. Unfortunately, the current was under 10 nA, and probably not worth pursuing. We also observed low SmH^- production from SmF_3 cathodes for about 15 minutes, probably due to absorbed water in the targets. The SmH^- current disappeared after the target was thoroughly heated in the sputter source.

The sesquioxide Sm_2O_3 would seem to be a good cathode material since it is relatively inert and easy to make. Lanthanide oxides are prepared by pyrolysis of insoluble lanthanide salts, often an oxalate, carbonate, nitrate, or sulphate [31]. Middleton observed unexpectedly poor current for SmO- using a solid samarium oxide cathode, however, and blamed it on ionizer poisoning [14]. Middleton suggested flowing

O_2 gas over a metallic Sm target, similar to his approach with H_2, to improve source output [14]. The simple chemistry of samarium oxide warrants investigation as a cathode, despite gloomy predictions of source output. SmO^- output from the LLNL source peaked at 30-50 nA, about 10% the output from SmF^-. We did not observe ionizer poisoning as noted by Middleton [14], with robust SmF- currents produced after sputtering Sm_2O_3 targets for a couple hours.

Since the molecular form of the cathode is destroyed in the sputtering process, we investigated the use of Sm_2O_3 doped with a high purity fluoride salt as a cathode to produce SmF^-. The oxide is easy to make at high purity and is relatively inert. It is also the starting material for the production of the fluoride. Mixing CaF_2, Sm_2O_3, and Nb metal at ratios of 1:1:1, 1:2:1, and 2:2:1 did produce some SmF^-, but currents were about the same as SmO^-.

Kinoshita *et al*. used a metallic target and an ECR source in their measurements of [146]Sm [32]. A metallic target is not likely to produce a good Sm- beam. Middleton also observed very low Sm- output, with hydrides producing much larger current, even when there was no H_2 gas feed [14]. We observed Sm^- currents of only 1-2 nA from both SmF_3 and Sm_2O_3 targets. The metal does not seem to be a promising target material for a negative ion source.

Spectrometer Operation

Spectrometer operational parameters will depend in part upon the quality and identity of the ion beam produced by the source and will vary among AMS facilities. The large number of potential isobars (Table 1) presents challenges in obtaining a clean background

for [146]Sm.   Both [149]Sm and [151]Sm will have relatively high concentrations in spent fuel, and will be amenable to current measurement in an off-axis Faraday cup. Based on the experience of Kinoshita *et al.* [32], it appears as though high energy and high positive charge state are needed to resolve [146]Sm from [146]Nd and other ions in the detector. But the ECR source and metal target may produce more interferences than a traditional AMS ion source.

It is likely that real applications will be sample limited, so measurement efficiency is an important consideration.   The need to operate at a reasonably well-populated charge state to make measurements will need to be balanced against the need for energy separation in the detector. We calculated stripping yield for a variety of terminal potentials on the LLNL FN accelerator. Operating at a terminal voltage of 9 MV yields a 21% conversion to the +11 charge state. Many of potential isobar and lighter ion scattering interferences can be removed through the use of the +11 charge state and multiple high energy (HE) filters. The specific operational parameters will vary with facility.

Conclusions

[146]Sm AMS is likely a niche measurement capability, requiring reasonable measurement efficiency due to limited samples but without the need for high sample throughput. TIMS and ICP-MS can routinely measure stable Sm isotopes now, often at part per million concentrations. Our modeling indicates that the limited production of [146]Sm over a wide dynamic range will produce isotopic ratios beyond measurement capabilities of these techniques and will require AMS. As in most new applications of

AMS, sample chemistry is probably more of a challenge than spectrometer operation. Of the potential target materials, SmF_3 seems most promising from ease of preparation and negative ion production. We believe the potential usefulness of the measurement warrants the development of $^{146}Sm/^{149}Sm$ and $^{146}Sm/^{151}Sm$ AMS.

Acknowledgements

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Figure Caption

Figure 1. Samarium isotope ratios after cooling predicted with ORIGEN models assuming long and short fuel cycles for a pressurized water reactor.
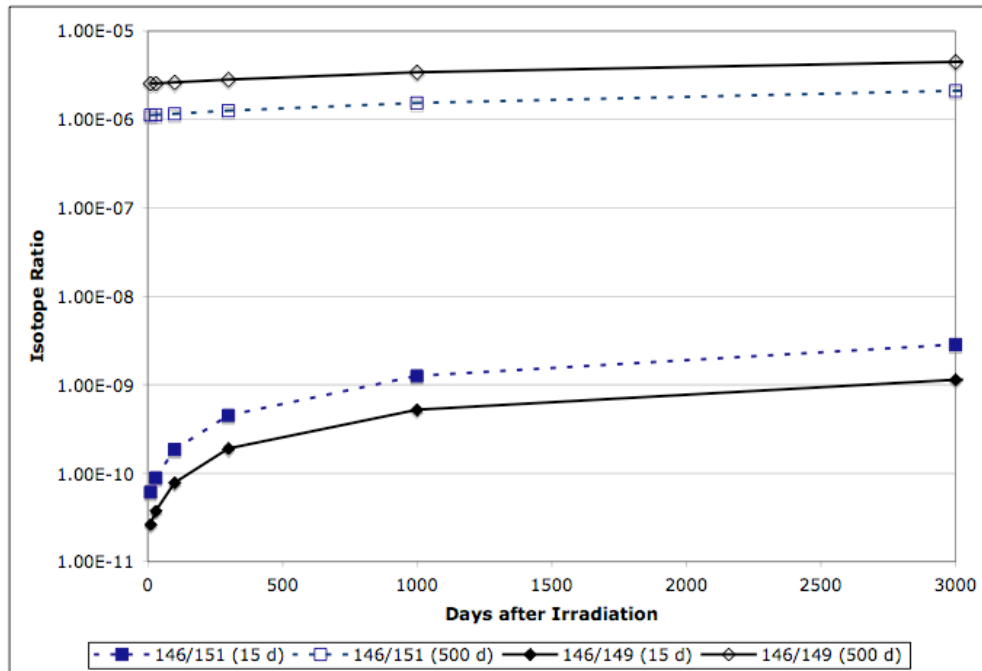
Table 1. Potential isobaric interferences for isotopes of Sm, Sm^{16}O and Sm^{19}F.

Mass	Desired Ion	Isobars
146	^{146}Sm	^{114}Sn^{16}O$_2$, ^{130}Ba^{16}O, ^{144}NdH$_2$, ^{145}NdH, ^{146}Nd, ^{145}PmH, ^{146}Pm, ^{144}SmH$_2$
149	^{149}Sm	^{117}Sn^{16}O$_2$, ^{133}Cs^{16}O, ^{132}Ba^{17}O, ^{133}Ba^{16}O, ^{148}NdH, ^{147}SmH$_2$, ^{148}SmH
151	^{151}Sm	^{119}Sn^{16}O$_2$, ^{133}Cs^{18}O, ^{134}Ba^{17}O, ^{135}Ba^{16}O, ^{150}NdH, ^{147}SmH$_4$, ^{151}Eu, ^{150}GdH
162	^{146}Sm^{16}O	^{143}Nd^{19}F, ^{145}Nd^{16}OH, ^{146}Nd^{16}O, ^{145}Pm^{16}OH, ^{145}Pm^{17}O, ^{146}Pm^{16}O, ^{162}Dy, ^{162}Er
165	^{149}Sm^{16}O	^{146}Nd^{19}F, ^{148}Nd^{16}OH, ^{146}Pm^{19}F, ^{148}Sm^{16}OH, ^{148}Sm^{17}O, ^{146}Sm^{19}F, ^{163}DyH$_2$, ^{164}DyH, ^{164}ErH
167	^{151}Sm^{16}O	^{150}Nd^{16}OH, ^{148}Sm^{18}OH, ^{149}Sm^{18}O, ^{150}Sm^{16}OH, ^{150}Sm^{17}O, ^{151}Eu^{16}O, ^{150}Gd^{16}OH, ^{150}Gd^{17}O, ^{165}HoH$_2$, ^{166}ErH, ^{167}Er
165	^{146}Sm^{19}F	^{146}Nd^{19}F, ^{148}Nd^{16}OH, ^{146}Pm^{19}F, ^{148}Sm^{16}OH, ^{148}Sm^{17}O, ^{149}Sm^{16}O, ^{163}DyH$_2$, ^{164}DyH, ^{164}ErH
168	^{149}Sm^{19}F	^{133}Cs^{35}Cl, ^{150}Gd^{18}O, ^{166}ErH$_2$, ^{167}ErH, ^{168}Er, ^{168}Yb
170	^{151}Sm^{19}F	^{133}Cs^{37}Cl, ^{152}Gd^{18}O, ^{154}Gd^{16}O, ^{151}Eu^{19}F, ^{170}Er, ^{169}TmH, ^{168}YbH$_2$, ^{170}Yb

Table 2. ^{152}Sm ion currents produced by various Sm cathode materials. All cathodes contained Nb powder to improve electrical and thermal conductivity.

Cathode	SmF$_3$				Sm$_2$O$_3$		Sm$_2$O$_3$ + CaF$_2$
Ion	Sm$^-$	SmH$^-$	SmF$^-$	SmF$_3^-$	Sm$^-$	SmO$^-$	SmF$^-$
Current (nA)	~1	<10	300	<10	~1	~30	~30